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FORM PTO-1390 U.S. DEI (REV 10-2000)	ATTORNEY'S DOCKET NUMBER								
TRANSMITTAL LETTE	TED STATES	P/37	81-4						
DESIGNATED/ELEC	U.S. APPLICATION NO). (If known, see 37 CFR 1.5)							
CONCERNING A FILING UNDER 35 U.S.C. 371 U9/8304									
INTERNATIONAL APPLICATION NO. INTERNATIONAL FILING DATE PRIORITY DATE CLAIMED 30 October 1998									
TITLE OF INVENTION PROCESS AND CONVERTER FOR THE PREPARATION OF AMMONIA									
APPLICANT(S) FOR DO/EO/US	Christia	n SPETH							
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information: This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. This is an express request to promptly begin national examination procedures (35 U.S.C. 371(f)). The US has been elected by the expiration of 19 months from the priority date (PCT Article 31). A copy of the International Application as filed (35 U.S.C. 371(c)(2)) a.									
d. have not been made at An English language translation of the An oath or declaration of the An Examination of the PCT Article 36 (35 U.S.C. 37	8. An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). 9. XX An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)) unsigned								
T=3	Items 11 to 16 below concern document(s) or information included:								
11. An information Disclosure St.	11. X An Information Disclosure Statement under 37 CFR 1.97 and 1.98.								
12. An assignment document for	recording. A separate of	over sheet in compliance	with 37 CFR 3.28	and 3.31 is included.					
13. A FIRST preliminary amendment.									
☐ A SECOND or SUBSEQUEN	A SECOND or SUBSEQUENT preliminary amendment. EXPRESS MAIL CERTIFICATE								
14. A substitute specification.				spondence is being					
15. A change of power of attorney	and/or address letter.	deposited with the Un Mail Post Office to A	ited States Postal	Service as Express					
16. XX Other items or information:	ET 612112672UC in an envelope addressed to								
2 sheets of draw Print EFS form.	ings.	On April 26 Dorothy of Name of Per	, 2001 .	respondence					
	all the second	April 26 Date of Sign							

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Total claims		20 =	0	X \$18.00	\$		
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P/3781-4

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of						
Christian SPETH	Date	: A	pril 26, 2001			
Serial No.:	al No.: Group Art Unit:					
Filed:	Exar	nine	er:			
For: PROCESS AND CONVERTER FOR THE PREP	ARATIC	N C	OF AMMONIA			
Asst. Commissioner for Patents				,		
Washington, D.C. 20231						
AMENDMENT/SUE	BMISSIC	ΟN				
Prior to examination, please amend the applicati	on as foll	lows	S .			
FEE CALCULATION						
Any additional fee required has been calculated:	as follow	s:				
If checked, "Small Entity" status	is claime	d.				
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AFTER PREVIOUSLY					ADDIT.	
AMENDMENT PAID FOR EXTRA P	RESENT		RATE		FEE	
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enclosed or if any additional fee during the prosecution	of this ap	plic	ation is not paid, th	ie Pa	atent	
Office is authorized to charge the underpayment to Depo						

CONTINGENT EXTENSION REQUEST

If this communication is filed after the shortened statutory time period had elapsed and no separate Petition is enclosed, the Commissioner of Patents and Trademarks is petitioned, under 37 C.F.R. §1.136(a), to extend the time for filing a response to the outstanding Office Action by the number of months which will avoid abandonment under 37 C.F.R. §1.135. The fee under 37 C.F.R. § 1.17 should be charged to our Deposit Account No. 15-0700.

AMENDMENTS

- _X_ If checked, amendment(s) to the specification and/or claims are submitted herewith.
- 1. ___ If checked, an abstract is submitted as the last page of Appendix A.

3. Claims:

Please amend claims 4 and 5 and add new claims 9 and 10 pursuant to 37 C.F.R. § 1.121(c)(i) as set forth in the "clean" version attached hereto as Appendix A. Entry is respectfully requested. A version with markings to show the changes made pursuant to 37 C.F.R. § 1.121(c)(ii) is attached hereto as Appendix B.

____ If checked, the optional complete set of "clean" claims pursuant to 37 C.F.R. § 1.121(c)(3) is attached hereto as Appendix C.

REMARKS/ARGUMENT

This Preliminary Amendment is being submitted to change the multiple dependent claims to single dependent claims in order to reduce the government filing fee.

EXPRESS MAIL CERTIFICATE

I hereby certify that this correspondence is being deposited with the United States Postal Service as Express Mail to Addressee (mail label # EL613112673US) in an envelope addressed to: Asst. Commissioner for Patents, Washington, D.C. 20231, on April 26, 2001:

Dorothy Jenkins

Name of Person Mailing Correspondence

April 26, 2001

Date of Signature

Respectfully submitted,

Edward A. Meilman

Registration No.: 24,735

OSTROLENK, FABER, GERB & SOFFEN, LLP

1180 Avenue of the Americas

New York, New York 10036-8403

Telephone: (212) 382-0700

APPENDIX A

"CLEAN" VERSION OF EACH PARAGRAPH/SECTION/CLAIM 37 C.F.R. § 1.121(b)(ii) AND (c)(i)

CLAIMS (with indication of amended or new):

- (Amended) 4. The process of claim 2, wherein the separation is obtained by cooling of the effluent stream and condensation of ammonia.
- (Amended) 5. The process of claim 2, wherein the separation is obtained by adsorption of ammonia contained in the effluent stream.
- (New) 9. The process of claim 3, wherein the separation is obtained by cooling of the effluent stream and condensation of ammonia.
- (New) 10. The process of claim 3, wherein the separation is obtained by adsorption of ammonia contained in the effluent stream.

APPENDIX B

VERSION WITH MARKINGS TO SHOW CHANGES MADE 37 C.F.R. § 1.121(b)(iii) AND (c)(ii)

CLAIMS:

- 4. The process of claim 2 [and 3], wherein the separation is obtained by cooling of the effluent stream and condensation of ammonia.
- 5. The process of claim 2 [and 3], wherein the separation is obtained by adsorption of ammonia contained in the effluent stream.

- 1 -

Process and Converter for the Preparation of Ammonia

The present invention relates to the preparation of ammonia by catalytic conversion of ammonia synthesis gas.

More particularly, this invention concerns synthesis of ammonia at high conversion rates of ammonia synthesis gas in presence of an ammonia synthesis catalyst arranged in a tubular reaction zone being cooled by a cooling agent on shell side of the tubular reaction zone. Synthesis of ammonia from synthesis gas of hydrogen and nitrogen is an exothermic process and the process requires cooling to obtain high conversion rates.

Even if the concentration of hydrogen and nitrogen in the synthesis gas is close to the stoichiometric composition for ammonia formation, complete reaction to ammonia cannot be obtained by a single passage of the synthesis gas through a catalytic bed. Furthermore, due to the exothermic nature of the ammonia synthesis, increasing temperature during passage through the catalytic bed displaces the equilibrium concentration towards lower ammonia concentration. Several methods for cooling the ammonia synthesis process are known.

The usual methods for the preparation of ammonia from synthesis gas employ either indirect or direct cooling of the synthesis gas between a number of catalytic beds, wherein the ammonia synthesis passes over an ammonia synthesis catalyst.

By direct cooling, cold synthesis gas is introduced into partly reacted synthesis gas between the beds. The disadvantage of this cooling method is dilution of the partly reacted gas with unreacted gas resulting in lower ammonia concentration in the product stream from the process.

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By the indirect cooling method, partly reacted synthesis gas is cooled by cold gas, usually fresh synthesis gas in a heat exchanger arranged between outlet and inlet of two catalyst beds.

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It has now been found that conversion rate of ammonia synthesis gas to ammonia is much improved when cooling the synthesis gas as it proceeds through a catalytic bed of ammonia synthesis catalyst by heat transfer to a cooling agent being in continuous heat contact with the process.

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Accordingly, this invention provides a process for the preparation of ammonia comprising steps of:

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contacting an ammonia synthesis gas with an ammonia synthesis catalyst arranged as reaction zone in one or more catalyst tubes;

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cooling the reaction zone continuously by transferring heat from the reaction zone to a cooling agent; and

withdrawing an ammonia rich effluent stream from the reaction zone.

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In its most general embodiment, the above process is carried out in a converter with one or more catalyst tubes arranged in a shell for retaining a cooling agent. Synthesis gas is introduced at top of the catalyst tube and passed through the reaction zone of an ammonia synthesis catalyst. Heat being developed during conversion of hydrogen and nitrogen contained in the synthesis gas to ammonia is continuously transferred through wall of the catalyst tube to the cooling medium surrounding the tube. By continuous cooling of the process, an adiabatic temperature

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increase is substantially avoided, so that the process is carried out at substantially isothermal conditions. Isothermal conversion of the synthesis gas results in higher conversion rates of the gas to ammonia than in the known ammonia synthesis processes with indirect or direct cooling of partially reacted synthesis gas, where the cooled gas is contacted with the catalyst at adiabatic conditions. Having removed heat of reaction from the reaction zone, the cooling medium is continuously or periodically withdrawn from the converter and externally cooled by e.g. heat exchange with water or steam and recycled to the converter by conventional means.

In a specific embodiment of the invention, the cooling agent is retained in a space formed by outer wall of the catalyst tube and inner wall of a cooling tube concentrically surrounding the catalyst tube.

As an advantageous feature of the latter embodiment, shell of a reactor with a number of catalyst tubes can be avoided or made from material with considerably lower mechanical strength than in the conventional ammonia converters.

Preferably, the cooling tubes surrounding the catalyst tubes are designed with a lower mechanical strength than the catalyst tube. In case of catalyst tube rupture reacting gas escaping at high pressure into the cooling tubes, ventilates into a space outside the cooling tube. Thereby, the synthesis gas depressurizes outside the cooling tubes and detrimental reactions of the gas with the cooling agent are avoided advantageously.

A further object of the invention is to provide a converter for the preparation of ammonia by reaction of ammonia synthesis gas in presence of an ammonia synthesis catalyst and

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cooling the reaction as it proceeds through the synthesis catalyst, the converter comprises at least one catalyst tube adapted to receive the ammonia synthesis gas and to hold a reaction zone with the ammonia synthesis catalyst, which at least one catalyst tube being arranged in a container with a cooling agent, as schematically shown in the attached Fig. 1.

Cooling media being useful as cooling agent in the above process and reactor will be any solid or liquid having a melting or boiling point below the desired temperature in the reaction zone, including salt or mixture of salts, metals or liquids being inert at the actual process conditions. Those cooling agents include eutectic mixtures of salts like mixtures of KNO3, NaNO3 and NaNO2 (supplied by Degussa) and eutectic mixtures of NaOH and KOH. Further eutectic salt mixtures and cooling liquids are well known in the chemical industry. The usual temperature condition in the above process will be between 300°C and 600°C. The temperature of the cooling agent has to be maintained at a predetermined level within the operation temperature range by external cooling of the agent as mentioned herein before.

Removal of ammonia from the ammonia rich product gas being withdrawn from the catalyst tubes is further an embodiment of the invention obtained through adsorption on an adsorbent having high affinity to ammonia at high pressure, such as regeneration of the spent adsorbent is carried out through depressurization of the adsorbent and recovery of ammonia rich gas similar to separation of e.g. oxygen or nitrogen in the known pressure swing adsorption processes. Furthermore, ammonia may be separated from unconverted synthesis gas by cooling and condensation of ammonia in the

ammonia rich effluent stream from the process. Unreacted synthesis gas being separated from ammonia in the product gas may then be recycled to the catalyst tube or passed to a subsequent catalyst tube for further conversion, as schematically shown in Fig. 2 and Fig. 3.

Example

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In a specific embodiment of the present invention a synthesis feed gas at a pressure of 13.8 MPa is preheated to 350°C and introduced to a reactor furnished with 600 reactor tubes with an inner diameter of 80.1 mm. The tubes were loaded with an upper portion of conventional iron ammonia catalyst and a lower portion of conventional ruthenium ammonia catalyst. Synthesis gas is distributed to the tubes and reacted over the ammonia catalyst. The catalyst tubes are surrounded by a shell. In the space between the shell and the tubes, a salt melt is being circulated countercurrently to the gas flow direction inside the tubes and in heat conducting relationship with the synthesis. Circulation of the salt melt serves to remove heat evolved from the exothermic ammonia synthesis reaction. The salt melt is introduced at 360°C into the cooling space and leaves the reactor at 420°C. The hot melt is cooled outside the reactor to 360°C in a heat exchanger, in which the heat desorbed from the salt melt is used for preheating of synthesis gas. The cooled salt melt is then pumped back to the reactor. Having passed through the catalyst reacted synthesis gas, being rich in ammonia, leaves the tubes and is withdrawn from the reactor. The gas is cooled by heat exchange with fresh synthesis gas.

In Table 1 below are listed the concentrations of the components in the gas stream inlet and exit the reactor as obtained by the above experiment.

Table 1

	Inlet gas	Exit gas
Composition (mole%):		
H ₂	73.59	52.95,
N ₂	25.37	18.73
Ar	0.36	0.45
CH₄	0.68	0.87
NH ₃		27.00
Pressure, MPa	•	13.4
Temperature, ^o C	13.8	402
	350	

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The inventive process may be employed in a one through ammonia synthesis section as well as in a more conventional type ammonia synthesis loop section or in combination with similar or other ammonia converter types in more advanced ammonia synthesis loop sections e.g. comprising feed gas converters and/or purge gas converters. The ammonia product may be retrieved from the ammonia rich product gas in the synthesis section by cooling and condensation of ammonia in the ammonia rich effluent stream or absorption. The removal of ammonia may be conducted in one or more stages, between and/or after each of the reaction zones.

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International Patent Application No. PCT/EP99/08055 Applicant: HALDOR TOPSOE A/S PCT 1083 – 00989/ej November 10, 2000

Claims 1 to 8

1. A process for the preparation of ammonia comprising the steps of

contacting an ammonia synthesis gas with an ammonia synthesis catalyst arranged as a reaction zone in one or more catalyst tubes;

cooling the reaction zone by a heat conducting relationship with a cooling agent; and

withdrawing an ammonia rich effluent stream from the reaction zone;

wherein the cooling agent is selected from salts, mixtures of salts and metals having a melting point below the temperature in the reaction zone.

- 2. The process of claim 1, wherein the ammonia synthesis gas is contacted with the ammonia synthesis gas arranged in two or more reaction zones with intermediate withdrawal of an ammonia rich effluent stream between the reaction zones.
- The process of claim 1, wherein the ammonia rich effluent stream is separated in a stream of unconverted ammonia synthesis gas and an ammonia product stream, the unconverted ammonia synthesis gas is recycled to the reaction zone.
- 4. The process of claim 2 and 3, wherein the separation is obtained by cooling of the effluent stream and condensation of ammonia.
- 5. The process of claim 2 and 3, wherein the separation is obtained by adsorption of ammonia contained in the effluent stream.

- 6. The process of claim 1, wherein the cooling agent is circulated within cooling tubes, each surrounding concentrically one catalyst tube.
- A converter for the preparation of ammonia comprising at least one catalyst tube adapted to receive ammonia synthesis gas and to hold a reaction zone of ammonia synthesis catalyst; and
 - at least one cooling tube concentrically surrounding the at least one catalyst tube and being adapted to hold the cooling agent selected from salts, mixtures of salts and metals having a melting point below the temperature in the reaction zone.
- 8. The converter of claim 7, wherein the wall of the cooling tube(s) has a lower mechanical strength than the wall of the catalyst tube(s).

ABSTRACT

Process and Converter for the Preparation of Ammonia

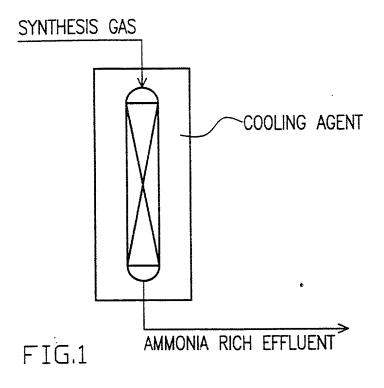
5 Process for the preparation of ammonia comprising steps of

contacting an ammonia synthesis gas with an ammonia synthesis catalyst arranged as reaction zone in one or more catalyst tubes;

cooling the reaction zone by heat conducting relationship with a cooling agent; and

withdrawing an ammonia rich effluent stream from the reaction zone.





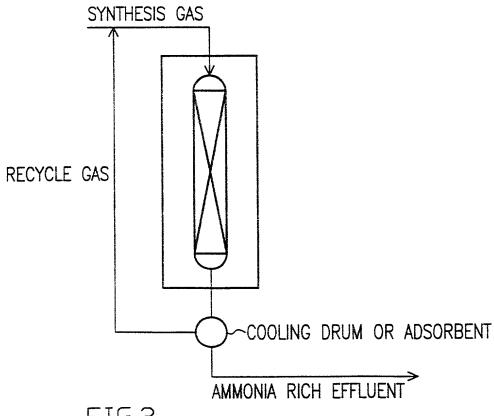


FIG.2

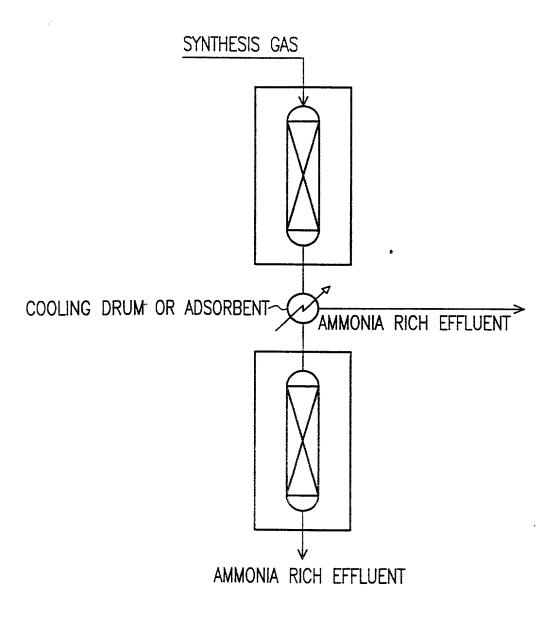


FIG.3

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<i>i</i> ,	As a below named inventor, I he verily believe that I am the original, subject matter which is claimed and PROCESS AND CONVE	reby declare that: my refirst and sole inventor (for which a patent is soil RTER FOR TI	esidence, post office if only one name is l ught on the invention HE PREPARA	address and citizensh isted below) or a joir entitled: ATION OF A	ip are as sta it inventor (i	ted below if plural in	next to my name; that I ventors are named) of the		
JUN 2 9	was filed on 25 OCTC	hereto, unless the follopber 1999 (EP99/08055) d and understand the content of th	as United Stat and was amended ontents of the above in to be material to patates Code §119 of adentified below any fed: N NUMBER	es patent Application on 10 Nover dentified specificatio tentability in accorda ny foreign application oreign application fo DATE 0 (day, max) 30 Octobe	Number or nber 2 n, including nce with Tit (s) for pater r patent or i F FILING nth, year)	PCT Inter 000 the claims dle 37, Coon nt or invén nventor's o	e of Federal Regulations, ator's certificate or United certificate having a filing PRIORITY CLAIMED UNDER 35 U.S.C. 119 YESX_NO YESNO		
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2 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	I hereby appoint customer no. 2352 OSTROLENK, FABER, GERB & SOFFEN, LLP, and the members of the firm, Samuel H. Weiner - Reg. No. 18,510; Jerome M. Berliner - Reg. No. 18,653; Robert C. Faber - Reg. No. 24,322; Edward A. Meilman - Reg. No. 24,735; Steven I. Weisburd - Reg. No. 27,409; Max Moskowitz - Reg. No. 30,576; Stephen A. Soffen - Reg. No. 31,063; James A. Finder - Reg. No. 30,173; William O. Gray, III - Reg. No. 30,944; Louis C. Dujmich - Reg. No. 30,625, Douglas A. Miro - Reg. No. 31,043, and Michael J. Scheer - Reg. No. 34,425, as attorneys with full power of substitution and revocation to prosecute this application, to transact all business in the Patent & Trademark Office connected therewith and to receive all correspondence.								
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1-02	FULL NAME OF SOLE OR FIRST INVENT Christian SPETH	INVENTORS SIGNATURE			23 may . 07				
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	Kirkevangen 33, DK-3540 Lynge, Denmark								
	FULL NAME OF SECOND JOINT INVENT	OR (if any)	INVENTOR'S SIGNA	TURE		DATE			
	RESIDENCE (City and either State or Foreign Country) COUNTRY OF CITIZENSHIP					ENSHIP			
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	FULL NAME OF THIRD JOINT INVENTO	INVENTOR'S SIGNATURE			DATE				
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